Several mechanisms were proposed and the reasons presented for rejecting them. A satisfactory mechanism was presented which was in agreement with all experimental facts. The main mechanism was represented by the reactions

$$n\text{-}C_3H_7I \rightleftarrows n\text{-}C_3H_7 + {}^1/_2I_2 \qquad \text{(equil.) (d-4)}$$
$$n\text{-}C_3H_7 + I_2 \longrightarrow \text{iso-}C_3H_7I + I \qquad \text{(slow) (d-5)}$$
$$\text{iso-}C_3H_7I \longrightarrow {}^1/_2C_3H_8 + {}^1/_2C_3H_6 + {}^1/_2I_2 \text{ (rapid) (d-6)}$$

The equilibrium for reaction (d-4) was calculated from the strength of the bonds involved and the entropies of the reactants. It is expressed by the equation

$$K = 1.22 \times 10^4\, e^{-24{,}700/RT} \left(\frac{\text{mole}}{\text{cc.}}\right)^{1/2}$$

The rate constant k_5 for reaction (d-5) was calculated as

$$k_5 = 1.79 \times 10^8 T^{1/2}\, e^{-12{,}600/RT} \left(\frac{\text{mole}}{\text{cc.}}\right)^{-1} \text{sec.}^{-1}$$

The study of the pyrolysis of *n*-butyl iodide in the temperature range of 590 to 622°K. showed that the reaction rate is similar to the decomposition of *n*-propyl iodide, exhibiting catalysis by iodine. However, no exact calculations of the rate could be made because the ratio of final to initial pressure of the decomposing gases varied when iodine was added to the *n*-butyl iodide initially. Thus the time-pressure measurements were not an accurate measure of the rate of disappearance of *n*-butyl iodide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Kinetics of the Thermal Decomposition of Isopropyl Iodide

BY J. L. JONES AND R. A. OGG, JR.

In a previous paper the kinetics of the thermal decomposition of *n*-propyl iodide and *n*-butyl iodide were discussed.[1] It was shown that the rate determining step for *n*-propyl iodide was given by the expression

$$\frac{-\mathrm{d}(C_3H_7I)}{\mathrm{d}t} = k(C_3H_7I)(I_2)^{1/2} \qquad (1)$$

The decomposition of *n*-butyl iodide resembled qualitatively that for *n*-propyl iodide, but it was not treated quantitatively due to a variation in the product composition with the amount of free iodine in the system. It was shown that the pyrolysis of *n*-propyl iodide could be explained by the mechanism

$$n\text{-}C_3H_7I \rightleftarrows {}^1/_2I_2 + n\text{-}C_3H_7\text{(equil.)} \qquad (2)$$
$$n\text{-}C_3H_7 + I \longrightarrow \textit{iso}\text{-}C_3H_7I\text{(slow)} \qquad (3)$$
$$\textit{iso}\text{-}C_3H_7I \longrightarrow C_3H_8 + C_3H_6 + {}^1/_2I_2\text{(rapid)} \qquad (4)$$
$$M + 2I \longrightarrow I_2 + M \qquad (5)$$

Reaction (3) is a slow reaction having an activation energy of 12.6 kcal./mole and a steric factor of 10^{-5}. This small steric factor is not surprising in view of the requirement of this reaction, *e. g.*, the transfer of a hydrogen atom from one carbon atom to another. The activation energy for this reaction is also in line with previous work.

Experimental Section

The isopropyl iodide was prepared according to the procedure of Bogart and Slocum[2] and the fraction boiling at 89.6° was used.

Homogeneity of the Thermal Decomposition.—Since the decomposition of *n*-propyl iodide and *n*-butyl iodide was proved to be homogeneous, it was not thought necessary to test this reaction for homogeneity. Ogg[3] likewise showed that the thermal decomposition of *s*-butyl iodide was homogeneous.

Apparatus and Procedure.—The apparatus and procedure have been described in a previous article.[1]

Experimental Results

Nature of Over-all Reaction.—As previously stated Glass and Hinshelwood[4] determined that the products of the reaction are propylene, propane and iodine in the proper ratio for the over-all reaction

$$2C_3H_7I \longrightarrow C_3H_8 + C_3H_7 + I_2 \qquad (6)$$

The average value of the ratio of final to initial pressure, P_∞/P_0, for this work was 1.49 and there was no trend of the ratio with the temperature of the reaction.

[1] Jones and Ogg, THIS JOURNAL, **59**, 1931 (1937).

[2] Bogart and Slocum, *ibid.*, **46**, 764 (1924).

[3] Ogg, *Trans. Faraday Soc.*, **31**, 482 (1934).

[4] Glass and Hinshelwood, *J. Chem. Soc.*, 1817 (1929).

Hydrogen iodide was detected as an end-product in the reaction, amounting to about 3% of the iodine concentration. Direct titration of the amount of iodine formed agreed with the results of Glass and Hinshelwood. In all runs tested, the products were completely condensed by liquid air, thus indicating the absence of appreciable amounts of hydrogen and methane.

Rate-Determining Step and Activation Energy.—A rate expression fitting the data was obtained by testing various types of empirical equations. The data fitted most closely a simple unimolecular expression

$$-d(C_3H_7I)/dt = k(C_3H_7I) \qquad (7)$$

The rate constant for each experiment was obtained by the standard procedure of plotting the value of log (C_3H_7I) against the time, on a very large scale, and drawing the best straight line through the experimental points. The plots gave straight lines over the first 70 to 85% decomposition and the terminal deviation from the straight line did not appear to depend greatly upon the temperature. Figure 1 gives a typical plot of log(C_3H_7I) *vs.* time. In general the rate constant appeared to fall off as the reaction proceeded to completion. Table I gives a complete set of rate constants for the thermal decomposition of isopropyl iodide. In order to determine whether these constants were independent of the initial iodide pressure, a series of rate constants determined in the vicinity of 591°K. were corrected to this temperature. The results are collected in Table II. They indicated that the rate constant had not fallen off at the lowest pressure studied, *e. g.*, 40 mm. Using the Arrhenius equation, the activation energy of the reaction was determined by plotting the logarithm of the rate constants against the corresponding values of $1/T$. From the slope of the best fitting line drawn through the experimental points (see Fig. 2), the activation energy was determined as 42,900 cal. The limit of error was about ±500 cal. The temperature independent factor for the rate constant equation is 1.59×10^{13}, a value well within the usual range of 10^{11} to 10^{15}. The temperature dependence of the rate constants is given by

$$k = 1.59 \times 10^{13} e^{-42,900/RT}$$

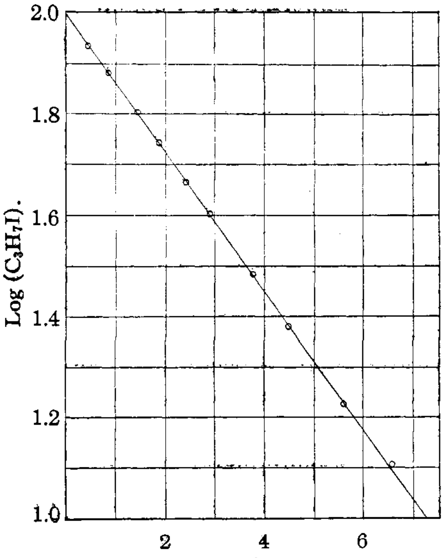

Fig. 1.—Kinetics of thermal decomposition of isopropyl iodide.

TABLE I

Run	Temp., °K.	$10^3/T$	$k \times 10^{-3}$, sec.$^{-1}$	$-\log k$	P_0, mm.
31	565.3	1.769	0.403	3.395	70.9
30	565.6	1.768	.463	3.334	199.8
28	565.9	1.767	.438	3.359	84.0
29	566.9	1.764	.442	3.355	37.0
33	571.8	1.749	.685	3.164	94.3
32	573.1	1.745	.710	3.149	46.2
8	580.5	1.763	1.220	2.914	99.0
9	581.4	1.720	1.200	2.921	50.5
10	581.7	1.719	1.200	2.921	162.3
11	581.7	1.719	1.240	2.907	144.3
12	581.7	1.719	1.19	2.925	87.2
35	589.3	1.697	2.00	2.699	110.2
34	590.2	1.694	1.92	2.717	62.5
13	590.5	1.693	2.04	2.690	82.4
14	590.8	1.693	2.10	2.677	74.2
15	590.9	1.692	2.19	2.660	40.6
17	591.0	1.692	2.29	2.640	117.6
16	591.0	1.692	2.22	2.654	122.1
23	598.7	1.670	3.63	2.440	138.6
22	599.1	1.669	3.83	2.417	65.5
18	599.5	1.668	3.70	2.432	74.4
19	599.8	1.667	3.47	2.460	122.8
20	600.1	1.666	3.47	2.460	46.1
21	600.2	1.666	3.67	2.435	91.0
24	604.0	1.656	5.25	2.280	96.4
27	605.2	1.652	5.13	2.290	71.7
25	605.3	1.652	5.25	2.280	36.0
26	608.6	1.643	6.52	2.186	248.4

TABLE II

ALL RATE CONSTANTS CORRECTED TO 591.0°K.

Run	P_0, mm.	$k \times 10^3$, sec.$^{-1}$
15	40.6	2.19
34	62.5	2.00
14	74.2	2.15
13	82.4	2.09
35	110.2	2.23
17	117.6	2.29
16	122.1	2.22

Discussion

Contrasting with the rate determining expression found for *n*-propyl iodide, a unimolecular rate of decomposition was found for the isopropyl iodide.

$$-\frac{d(C_3H_7)}{dt} = k(C_3H_7I)$$

The first mechanism presented below is similar in some steps to the mechanism proposed for the thermal decomposition of *s*-butyl iodide.[3]

Mechanism (a)

$$iso\text{-}C_3H_7I \longrightarrow iso\text{-}C_3H_7 + I \qquad \text{(a-1)}$$
$$iso\text{-}C_3H_7 + iso\text{-}C_3H_7I \longrightarrow C_3H_8 + C_3H_6I \qquad \text{(a-2)}$$
$$C_3H_6I \longrightarrow C_3H_6 + I \qquad \text{(a-3)}$$
$$M + 2I \longrightarrow I_2 + M \qquad \text{(a-4)}$$

Reaction (a-1) is considered to be the slow rate-determining step, followed by the rapid steps (a-2) and (a-3). The trimolecular recombination of iodine atoms is represented by equation (a-4).

The experimentally determined unimolecular rate constant at 600°K. (middle of the experimental temperature range) is 3.74×10^{-3} sec.$^{-1}$. This value compares favorably with the unimolecular rate constant 3.98×10^{-3} sec.$^{-1}$ for the decomposition of *s*-butyl iodide at the same temperature. One should expect similar unimolecular rate constants for the two compounds due to their closely related molecular structures.

Assuming that the carbon–iodine bond is broken in the primary reaction (a-1), one may calculate the temperature independent factor (*A*-factor) for the unimolecular rate constant from the theory of Rice and Gershinowitz.[5] The "*A*-factor" is considered to be a product of two parts, a "collision factor" A' which takes into consideration the one degree of vibrational freedom of the bond which breaks, and the "steric factor" A'' which consider all other degrees of freedom involved in the reaction. For our purpose we shall consider the steric factor A'' to be unity, and A' is given by

$$A' = ekT/hE'$$

where e is the base of the natural logarithms, k is the Boltzmann constant, T is the absolute temperature, h is the Planck constant, and E' is given by

$$E' = x(e^x - 1)^{-1} - \ln(1 - e^{-x})$$

x is defined as $(h\nu_i/kT)$, in which ν_i is the frequency of the vibration along the bond which breaks in the unimolecular reaction. Assuming that ν_i is 500 cm.$^{-1}$, the frequency which is associated with the carbon–iodine bond in the alkyl iodides, then the value of E' is 1.45×10^{13} at 600°*K*. This agrees with the experimental value of 1.59×10^{13}.

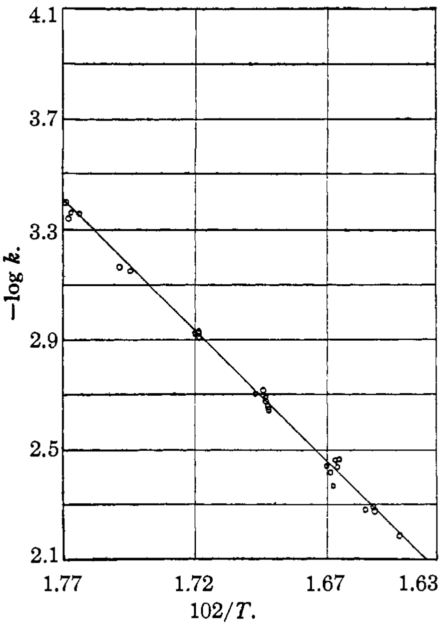

Fig. 2.—Kinetics of thermal decomposition of isopropyl iodide.

The experimentally determined activation energy of 42,900 calories may be considered as too high in comparison with the value of the activation energy of the unimolecular decomposition of *s*-butyl iodide, *i. e.*, 39,400 calories. In view of the close structural relation of the two iodides, one would expect the activation energies for the unimolecular reactions to be somewhat nearer. However, if one considers that the experimental errors of the activation energies are about 1000 and 500 calories for *s*-butyl and isopropyl iodides, respectively, then the difference becomes reasonable. Eucken[6] gives 44,000 calories as the heat of dissociation of the carbon–iodine linkage. Ogg[7] calculated a similar value from the data on heats of combustion of aliphatic iodides and the values of Kistiakowsky and Gershinowitz for the strength of the carbon–carbon bond (77,000 calories) and the carbon–hydrogen bond (94,000 calories). A value of the heat of dissociation of the carbon–iodine linkage, *i. e.*, 40,000 calories, was calculated from the heat of dissociation of the reaction

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[5] Rice and Gershinowitz, *J. Chem. Phys.*, **2**, 853 (1934).

[6] Eucken, "Lehrbuch der chemischen Physik," Akademische Verlagsgesellschaft, Leipzig, 1930.

[7] Ogg, THIS JOURNAL, **56**, 532 (1934).

ICN $\longrightarrow \frac{1}{2}I_2 + \frac{1}{2}(CN)_2$ and from the dissociation of cyanogen.

A second criticism of this mechanism is due to the necessity of assuming that the reaction

$$iso\text{-}C_3H_7I + I \longrightarrow I_2 + iso\text{-}C_3H_7$$

is very slow while the closely related *s*-butyl iodide decomposes by this equation. The definite falling off of the unimolecular rate constant in the individual experiments on isopropyl iodide (after about 70% decomposition) indicates that the above equation certainly plays a negligible part in this mechanism.

Mechanism (b).—A second mechanism proposed for the pyrolysis of isopropyl iodide will now be discussed.

$$iso\text{-}C_3H_7I \longrightarrow C_3H_6 + HI \qquad \text{(b-1)}$$
$$HI + iso\text{-}C_3H_7I \longrightarrow C_3H_8 + I_2 \qquad \text{(b-2)}$$

The rate determining step is the splitting off of hydrogen iodide from the isopropyl iodide and the simultaneous rearrangement of the electronic structure of the propylidene radical to form propylene. It is followed by the rapid reduction of the isopropyl iodide by the hydrogen iodide.

The slightly high activation energy would be explained by this mechanism, for (b-1) could very well have such an activation energy. Since no catalysis of the decomposition by iodine is involved in this mechanism, this mechanism is valid in this respect.

If isopropyl iodide is closely related to *s*-butyl iodide, which was used as the basis of an argument against mechanism (a), then one would expect that *s*-butyl iodide would also decompose in part by the mechanism given above. No indication of mechanism (b) was found by Ogg in his study of *s*-butyl iodide.

The rate constant for the unimolecular decomposition of isopropyl iodide at 600°K. is 3.74×10^{-3} sec.$^{-1}$. If one considers that a maximum concentration of hydrogen iodide of 5 mm. is produced by the above mechanism (above experimental maximum), then by using the rate constant for the bimolecular reaction of *n*-propyl iodide and hydrogen iodide one obtains a calculated unimolecular rate constant of 5.04×10^{-4} sec.$^{-1}$. Since the rate constant of Ogg[1,7] from which this reduction rate is calculated is too large by an error of ten-fold, it is necessary to assume that the reduction of the isopropyl iodide by hydrogen iodide is at least 1000-fold faster than the measured reduction rate of *n*-propyl iodide if the above mechanism is to be valid. While such a great difference in the rates of reduction of the two iodides is possible, it does not seem to be very likely. However, further experimental work is needed on this point.

Summary

An experimental study was made of the kinetics of the thermal decomposition of isopropyl iodide in the temperature range 565 to 609°K. The rate is represented by

$$-\frac{d(C_3H_7I)}{dt} = k(C_3H_7I)$$

The temperature dependence of the rate constant is given by

$$k = 1.59 \times 10^{13} e^{-42,900/RT} \text{sec.}^{-1}$$

Two mechanisms were suggested to account for the over-all reaction, but there was not sufficient evidence to make a definite decision relative to them.

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